

AD-A253 644



## DOCUMENTATION PAGE

Form Approved

OMB No. 0704-0188

2

ation is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson 02, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

2. REPORT DATE July 6, 1992		3. REPORT TYPE AND DATES COVERED Technical Report	
4. TITLE AND SUBTITLE Strong Exchange Coupling Between the Lanthanide Ions and Phthalocyaninato Ligand Radical in Bis(phthalocyaninato)lanthanide Sandwich Compounds		5. FUNDING NUMBERS N00014-92-J-1637	
6. AUTHOR(S) Kathleen L. Trojan, Jonathan L. Kendall, Keith Kepler and William E. Hatfield			
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Chemistry - Campus Box 3290 The University of North Carolina at Chapel Hill Chapel Hill, NC 27599-3290		8. PERFORMING ORGANIZATION REPORT NUMBER Technical Report 45	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) Department of the Navy Office of the Chief of Naval Research 800 N. Quincy Street, Code 1513:RKL Arlington, VA 22217-5000		10. SPONSORING/MONITORING AGENCY REPORT NUMBER	
11. SUPPLEMENTARY NOTES Accepted for Publication in INORGANICA CHIMICA ACTA			
12a. DISTRIBUTION AVAILABILITY STATEMENT Distribution Unlimited This document has been approved for public release and sale; its distribution is unlimited.		12b. DISTRIBUTION CODE DTIC ELECTE JUL 23 1992 S A D	
13. ABSTRACT (Maximum 200 words) A series of lanthanide phthalocyanine sandwich compounds with the formula $[(Pc^{2-})Ln^{III}(Pc^{1-})]$ have been synthesized and characterized. To a first approximation, the lanthanide ions exist in their normal trivalent state, while one of the phthalocyanine ligands exists in the normal dianionic state and the other exists as a monoanionic phthalocyanine radical. It is obvious from the magnetic behavior of these compounds that there is a strong magnetic interaction between the lanthanide f-electrons and the phthalocyanine radical electron. Both antiferro- and ferromagnetic ground states have been observed in this series of compounds which depends on the symmetry and occupancy of the magnetic orbitals on the lanthanide ion. In some cases both the antiferro- and ferromagnetic states of a single system are observed in the temperature range studied. In these cases, the energy separation between states has been evaluated from the magnetic data.			
14. SUBJECT TERMS lanthanide phthalocyanines sandwich compounds antiferromagnetic ferromagnetic magnetism		15. NUMBER OF PAGES 36 16. PRICE CODE	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT Unlimited

OFFICE OF NAVAL RESERACH

Contract N00014-92-J-1637

R&T Code 4135007---08

TECHNICAL REPORT NO. 45

**Strong Exchange Coupling Between the Lanthanide Ions and  
Phthalocyaninato Ligand Radical in  
Bis(phthalocyaninato)lanthanide Sandwich Compounds**

by

Kathleen L. Trojan, Jonathan L. Kendall,

Keith Kepler and William E. Hatfield

The Department of Chemistry, The University of North  
Carolina at Chapel Hill, North Carolina, 27599-3290, U.S.A.

Prepared for Publication in

**INORGANICA CHIMICA ACTA**

Reproduction in whole or in part is permitted for  
any purpose of the United States Government

\*This document has been approved for public release  
and sale, its distribution is unlimited.

\*This statement should also appear in Item 3 of Document Control  
Data - DD Form 1473. Copies of the form are available from the  
cognizant contract administrator.

**92-19604**



92 7 22 006

# Strong Exchange Coupling Between the Lanthanide Ions and Phthalocyaninato Ligand Radical in Bis(phthalocyaninato)lanthanide Sandwich Compounds

KATHLEEN L. TROJAN, JONATHAN L. KENDALL<sup>#</sup>, KEITH D. KEPLER<sup>+</sup>  
AND WILLIAM E. HATFIELD<sup>\*</sup>

*Department of Chemistry, University of North Carolina at Chapel Hill,  
Chapel Hill, North Carolina 27599-3290 (U. S. A.)*

## Abstract

A series of lanthanide phthalocyanine sandwich compounds with the formula  $[(Pc^{2-})Ln^{III}(Pc^{1-})]$  have been synthesized and characterized. To a first approximation, the lanthanide ions exist in their normal trivalent state, while one of the phthalocyanine ligands exists in the normal dianionic state and the other exists as a monoanionic phthalocyanine radical. It is obvious from the magnetic behavior of these compounds that there is a strong magnetic interaction between the lanthanide f-electrons and the phthalocyanine radical electron. Both antiferro- and ferromagnetic ground states have been observed in this series of compounds which depends on the symmetry and occupancy of the magnetic orbitals on the lanthanide ion. In some cases both the antiferro- and ferromagnetic states of a single system are observed in the temperature range studied. In these cases, the energy separation between states has been evaluated from the magnetic data.

<sup>#</sup>Current Address: Department of Chemistry, Stanford University, Stanford, CA

<sup>+</sup>Current Address: Department of Chemistry, University of Illinois, Urbana, IL

Codes

for

Journal Special  
A-1

## Introduction

A variety of tetraazamacrocycles, such as the phthalocyanines, porphyrins and their derivatives have been extensively studied in order to model the behavior of naturally occurring porphyrinic macrocycles [1]. These compounds play an important role in biological processes, such as transport and storage of oxygen, nitrogen fixation, and photosynthesis. Due to the propensity of high coordination, in this case octacoordination of the lanthanide ions, these ions are able to accommodate two tetraazamacrocycles in a sandwich like structure around the lanthanide ion. Compounds in which two porphyrin disks are held together at a fixed distance by a large rare earth cation could serve as models for energy transfer in biological systems [2].

Lanthanide phthalocyanine sandwich compounds with the formula  $\text{Ln}(\text{Pc})_2$  have been known for over twenty-five years [3]. To a first approximation, the lanthanide ion has a formal oxidation state of +3, with one of the phthalocyanine ligands having a charge of -2, while the second phthalocyanine ligand may be considered to be a singly oxidized radical with a charge of -1. The crystal structure of  $[\text{Lu}(\text{Pc})_2] \cdot \text{CH}_2\text{Cl}_2$  has been determined by Weiss et. al. [4] Other lanthanide sandwich compounds have essentially the same structure [5] in which the two phthalocyaninato rings are rotated approximately  $45^\circ$  with respect to one another, and it is assumed that the compounds described here have the same structure. Powdered samples of the compounds used in this study were verified by their ultraviolet, visible and near-infrared spectra and by elemental analysis.

## Experimental

### *Synthesis*

The lanthanide phthalocyanines were prepared by a method similar to those which are described in the literature [6-8]. Excess 1,2-dicyanobenzene (recrystallized from methanol) was mixed in an approximately 14:1 molar ratio with the appropriate lanthanide acetate and vigorously ground together by using a mortar and pestle. The mixture was then placed in a large reaction tube equipped with a water cooled condenser, heated in a sand bath at 280-300°C for 4-5 hours and cooled slowly. Unreacted dicyanobenzene collected on the sides of the reaction tube and condenser. The dark green product which formed was separated from the unreacted dicyanobenzene and reground. The product was then returned to a clean, dry reaction tube and heated in a sand bath at 300°C under vacuum for 12-24 hours. This process was repeated several times. The product was washed with acetic anhydride and cold acetone, dissolved in a minimum amount of chloroform and gravity filtered to remove any free phthalocyanine which may have formed. This solution was separated on a 15 x 2 inch basic alumina column using a 5% methanol/toluene solution. In most cases, a green fraction eluted first, followed by a blue fraction. Some blue product remained on the top of the column and could not be eluted. Occasionally, a small amount of brown product could be detected which was previously determined [5] to be the linear polymer of 1,2-dicyanobenzene. The ratio of blue and green products obtained depended on the lanthanide used, such that as one moves to the left of the periodic table, more blue product is formed. The solution containing the green product was taken to dryness on a rotary evaporator and then dried in

a vacuum oven. Although there has been much debate concerning the composition of these compounds [8-13], it has been determined that the green compound is of the composition most readily depicted, to a first approximation, as  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Pc}^{1-})$ , where Ln equals Pr, Gd, Tb, Dy, Ho, Er, Tm, Yb or Lu,  $(\text{Pc}^{2-})$  is the dianionic form of the phthalocyaninato ligand and  $\text{Pc}^{1-}$  is the monoanionic radical form of the phthalocyaninato ligand. It has been discussed in the literature that there are two blue compounds that also evolve from this synthesis [7], namely,  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Pc}^{2-})\text{H}$  and  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Ac}^{1-})$  where  $(\text{Ac}^{1-})$  is the monoanionic acetato ligand. It has been shown that the blue compound that elutes is the  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Pc}^{2-})\text{H}$  compound [13] and it is assumed that the blue compound that remains on top of the column is the  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Ac}^{1-})$  compound. However, these compounds were not studied in this research. As discussed in the literature [2], the temperature at which the initial reaction occurs has a large effect on the products formed. It was seen that if the reaction temperature deviated by 20 degrees or more above 300°C, very little green product was obtained and the major product formed was a blue material which could not be eluted from the column and was assumed to be the  $(\text{Pc}^{2-})\text{Ln}^{3+}(\text{Ac}^{1-})$  blue form.

### *Physical Measurements*

Low temperature magnetic susceptibility data were collected in the temperature range of 4.2 to 100 K using a Princeton Applied Research model 155 vibrating sample magnetometer (VSM) equipped with a Janis Research Company model 153 liquid helium cryostat. Magnetic fields between 0 and 15 kOe were generated using a Magnion model H-96 electromagnet and a Magnion

model HSR-1365 power supply. The magnetic field was regulated using a Magnion model FFC-4 field control unit and a Rawson-Lush model 920 MCM rotating coil gaussmeter. The magnetic field was periodically calibrated against lithium and proton NMR resonances using a Walker/Magnion Model G-502 NMR gaussmeter. The sample temperature was monitored by using either a gallium-arsenide or gallium-aluminum-arsenide diode, which were purchased and calibrated by Lake Shore Cryotronics. The magnetometer signal output was calibrated using the standard, mercury tetrathiocyanatocobaltate(II),  $\text{HgCo(NCS)}_4$  [14-16]. Powdered samples were packed into precision milled Lucite sample holders. Diamagnetic corrections of constituent atoms were made using Pascal's constants [17-18].

High temperature magnetic susceptibility data in the range of 77 K to 300 K were collected using a Faraday balance. The Faraday system is comprised of a Cahn 2000 electrobalance, an ANAC series 3472 100 mm electromagnet, an ANAC Model 3610-I magnet control system and a Sorenson SRL 40-50 power supply. A magnetic field of  $\approx 7500$  G was used for all measurements with a field gradient of  $\approx \pm 160$  G/cm generated by Georges Associates Model 502 Lewis coils and the associated Georges Associates Model 202 power supply. A liquid nitrogen dewar of local design was placed around the sample tube containing the He static exchange gas. The sample was allowed to warm slowly to room temperature and data were collected automatically. The sample temperature was monitored using a calibrated Lake Shore Cryotronics DT-500 silicon diode located approximately 7 mm below the sample. The magnetometer signal output was calibrated using  $\text{HgCo(NCS)}_4$ . The samples were contained in polycarbonate capsules obtained from Universal Plastics and Engineering Company and

suspended from the electrobalance using a chain made of fine quartz tubing and fine gold chain. Diamagnetic corrections of constituent atoms were made using Pascal's constants.

Electron paramagnetic resonance (EPR) spectra were obtained using a Varian E-109 spectrometer system operated at X-band. The frequencies were monitored using a Hewlett-Packard Model 5340 A frequency counter. Low temperature EPR spectra were obtained using an Oxford Model ESR-910 continuous flow cryostat equipped with a AuFe/chromel thermocouple. The field was calibrated using the standard, diphenylpicrylhydrazyl (DPPH). Samples were contained in capillary tubes placed inside quartz sample tubes.

The data were fit to theoretical models using a Simplex [19-21] non-linear least squares fitting routine. The function minimized was the sum of the squares of the residuals

$$R = \sum [ (Q_i^{\text{obsv}} - Q_i^{\text{calc}})^2 / (Q_i^{\text{obsv}})^2 ] \quad (1)$$

where  $Q_i$  is the physical quantity being fit.

## Results and Discussion

### *Spectroscopic and Structural Properties*

The electronic spectra of the lanthanide bis(phthalocyanine) compounds have been thoroughly studied [6-8,13,22]. The results of these investigations have been used in this research to verify the composition of the products. The



electronic spectra of these compounds reflect the individual transitions expected for the dianionic and monoanionic radical forms of phthalocyanine as well as an intervalence charge transfer band which accounts for the interaction between phthalocyanine species. The values of the ultraviolet, visible and near infrared transitions for the lanthanide bis(phthalocyanine) compounds are given in Table 1.

By comparison of the powder patterns of the  $\alpha$ ,  $\beta$  and  $\gamma$  phases for  $\text{NdPc}_2$  given by Darovskikh [23], the powder patterns of the compounds studied in this research very closely resemble those of the  $\gamma$  phase. From the structures given, it is assumed in this work that the lanthanide bis(phthalocyanine) sandwich compounds form a slightly distorted square antiprism with an angle of rotation of  $\approx 41\text{-}42^\circ$ . The metal to  $\text{N}_4$  plane distances are not equivalent between the lanthanide ion and the two phthalocyanine rings. The average values of these distances range from  $\approx 1.34 \text{ \AA}$  for  $\text{LuPc}_2$  to  $\approx 1.50 \text{ \AA}$  for  $\text{PrPc}_2$ . Both phthalocyanine rings are curved away from the lanthanide ion, however, it is likely that one phthalocyanine ligand is more distorted than the other [24] due to the inequality of the two ligands.

### *Magnetic Properties*

Three possibilities exist for the type of interaction between the lanthanide f-electrons and the ligand based radical electron. The most obvious choice is that no interaction exists between the two and each behaves independently in terms of contribution to the magnetic susceptibility of the complex. It is also possible that these two species can interact either antiferromagnetically or ferromagnetically. In the case where no interaction exists, the magnetic susceptibility of the complex

would be represented by:

$$\chi_m = \frac{N\beta^2}{3kT} [g_L^2 J(J+1) + g_e^2 S(S+1)] , \quad (2)$$

and the magnetic moment would be calculated using the equation:

$$\mu_{\text{eff}} = [g_L^2 J(J+1) + g_e^2 S(S+1)]^{1/2} , \quad (3)$$

where  $g_e$  is the free-electron g-value equal to 2.0023.

The values of  $\mu_{\text{eff}}$  for all of the trivalent lanthanides discussed have been calculated using the free ion term and the free ion plus radical term as discussed above. These values were compared to the limiting values found experimentally and are given in Table 2. Since, the majority of the complexes studied show an approximately 1 B.M. reduction from that of the free-ion value, it is obvious that the lanthanide f-electrons and the ligand based radical electron do indeed interact. Based on the magnitude of the moment reduction, as discussed below, this interaction is very strong.

A model of the energy level splitting for the lanthanide ion including a strong interaction with the phthalocyanine radical is shown in Figure 1, with  $\text{Yb}^{3+}$  as the example. The relative order of perturbations to the free ion are now given by:

$$e^2/r_{ij} \geq \lambda L \cdot S \gg J > V_{\alpha} \approx kT,$$

where  $J$  represents the coupling between the lanthanide free ion ground state term and the phthalocyanine radical electron. Due to the strength of this

interaction, it is possible to calculate a new term symbol for all of the complexes based on a linear combination of the  $^{2S+1}L_J$  term of the lanthanide and the  $^2S_{1/2}$  term of the ligand radical. For an antiferromagnetic interaction, this new term would be  $^{2S}L_{J-1/2}$ , for gadolinium through lutetium where  $J = L + S$ . Similarly for the ferromagnetically coupled state this new term would be designated  $^{2S+2}L_{J+1/2}$ , where  $S$  and  $J$  are the free ion values for the ground state of the lanthanide ion in question. In the case of praseodymium, where  $J = L - S$ , the new terms would be designated as  $^{2S}L_{J+1/2}$  and  $^{2S+2}L_{J-1/2}$ , for the antiferromagnetic and ferromagnetically coupled states, respectively. As illustrated in Figure 1, depending on the magnitude of the antiferromagnetic-ferromagnetic splitting,  $\Delta E$ , it is possible for the ferromagnetically coupled state to become populated at high temperatures.

From the Van Vleck equation given previously, the magnetic susceptibility for these complexes including both antiferromagnetic and ferromagnetic states can be given by the expression (equation 4):

$$\chi = \frac{N\beta^2}{kT} \left\{ \frac{\sum_j (m_{i_0} g_{i_0})^2 + \sum_j (m_{j_1} g_{j_1})^2 \exp\left(\frac{-\Delta E}{kT}\right)}{(2J_0 + 1) + (2J_1 + 1) \exp\left(\frac{-\Delta E}{kT}\right)} \right\}$$

For simplicity, it is assumed that all multiplet states are equally populated, since the crystal field splitting is assumed to be small in this case. The new ground state energy is set equal to zero and the new excited state energy is set equal to

$\Delta E$ , so the the relative energy separation between the two states can be determined. The first order Zeeman terms  $E_n^1$  are equal to  $m_j g_j \mu_B$  and second order Zeeman terms are neglected. The following is a detailed description of the magnetic behavior for each of the lanthanide bis(phthalocyanine) compounds studied. The experimental magnetic susceptibility data, given in units of  $\mu_{\text{eff}}$  versus temperature, for all of the lanthanide bis(phthalocyanine) compounds studied are given in Figure 2.

#### *i) Praseodymium*

From the experimental data, taken from 4.2 to 300 K, it can be seen that the limiting moment at 300 K is equal to  $\approx 2.5$  B.M. The data was therefore fit to the Curie-Weiss model as follows:

$$\chi_m = \frac{N g_L^2 \beta^2 [J(J+1)]}{3k(T - \theta)} \quad (5)$$

where  $J$  was input as a constant and the data was fit using a non-linear Simplex least squares fitting routine, as described earlier, to  $g$  and  $\theta$ . Here  $\theta$  is the Weiss constant which corrects for the less than ideal circumstances imposed by the Curie law alone. With  $J$  equal to  $7/2$  the data was fit with the parameters  $g=0.65$  and  $\theta=-34.64$  K with an R-value for the fit of 0.0244.

The fit to the data was approached from several different directions. Attempts to fit the data using a  $J$  value other than  $7/2$  did not give reasonable fits. When  $J$  was set at  $7/2$ , all fits converged with the same set of parameters as those given above, regardless of the initial parameters input. Therefore, it may be concluded that the parameters for the best fit to the data are given above and

are not simply the result of a local minimum. Praseodymium is unique in that it is the only example in the series of compounds studied in this work where the ground state is that which results from the ferromagnetic coupling of the lanthanide and ligand electrons. An explanation of this interaction will be discussed in the following section.

## *ii) Gadolinium*

From the experimental data taken from 4.2 to 100 K, it can be seen that the moment levels off at  $T < 10\text{ K}$  with a value of 6.9 B.M. which remains constant up to 100 K. Since it is well known that compounds of trivalent gadolinium almost always obey the Curie law and provide, by far, the best examples of the free ion model, several attempts were made to fit this data to the Curie-Weiss equation given previously.

All attempts to fit the data to the Curie-Weiss law with  $J=7/2$  and  $g=2.00$  were fruitless. With  $J=3$ , and  $g$  fixed at 2.00, a value of  $\theta = -0.47\text{ K}$  was obtained with an R-value for the fit of 0.0122. When all parameters were allowed to vary, the parameters obtained were  $g=2.01$  and  $\theta = -0.51\text{ K}$  with an R-value of 0.0118. Both fits show excellent agreement to the data and appear to be equivalent within the limits of error. Therefore, it can be concluded that the ground state for  $\text{GdPc}_2$  is a  $^7\text{S}_3$  state which arises from the strong antiferromagnetic coupling between the gadolinium f-electrons and the phthalocyanine radical electron. The ferromagnetically coupled  $^9\text{S}_4$  excited state does not contribute to the magnetism of this compound in the temperature range studied.

*iii) Terbium*

From the experimental data taken from 4.2 to 300 K, it can be seen that the magnetic moment levels off near 8.6 B.M. Initially, only the data from 0-100 K obtained from the vibrating sample magnetometer were used in the SIMPLEX fitting routine. From this set of data, with  $J=11/2$ , the best fit values obtained using the Curie-Weiss equation were found to be  $g=1.46$  and  $\theta=-1.54$  K with an R-value of 0.0201. When the experimental data from 77-300 K obtained from the Faraday balance were combined with this data, the new best fit parameters were found to be  $g=1.45$  and  $\theta=-1.45$  K with an R-value of 0.0230. Both show excellent agreement with the experimental data and appear to be equal within experimental error.

All attempts to fit the data with J-values other than 11/2 were unsuccessful. The values for  $g$  and  $\theta$  were allowed to vary freely during the SIMPLEX fitting routine, and these parameters always converged to the same values as those given above. Therefore, for the case of  $\text{TbPc}_2$ , it is obvious that the ground state of the complex is  ${}^6\text{F}_{11/2}$ , a state which arises from strong antiferromagnetic coupling between the terbium f-electrons and the phthalocyanine radical electron. The  ${}^8\text{F}_{13/2}$  excited state, which arises from the ferromagnetic coupling as described previously, does not appear to contribute to the magnetism in the temperature range studied.

*iv) Dysprosium*

The experimental data taken from 4.2 to 300 K does not follow simple

Curie-Weiss behavior. At very low temperatures (4.2 to 60 K), the data can be fit to the Curie-Weiss law with  $J=7$ ,  $g = 1.30$  and  $\theta = -2.68$  K. However, above this temperature, deviations are evident. Due to the inability to fit the data for  $J=7$ , many attempts were made to fit the data to the  ${}^6\text{H}_{15/2}$  state, with and without the presence of the ligand radical electron. All attempts were unsuccessful, ruling out all other possibilities considered. Thus the data were fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state as given by equation 4 and depicted in Figure 1.

This model does not fit the data at very low temperatures, since the model assumes for simplicity that all  $m_j$  states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 40 K the data can be fit to this model with  $J_0=7$ ,  $J_1=8$ ,  $g_0$  and  $g_1$  fixed at 1.29 and 1.375, respectively, and  $\Delta E$  equal to  $216\text{ cm}^{-1}$ . This fit gave an R-value of 0.00227 with  $T_{\min}$  set at 40 K. Dysprosium bis(phthalocyanine) is the first compound in the series discussed that shows the presence of the ferromagnetically coupled excited state and lends further credence to the model of the magnetic behavior proposed.

#### v) Holmium

From the experimental data taken from 4.2 to 300 K, it can be seen that the magnetic moment levels off near 9.5 B.M. The best fit values obtained using the Curie-Weiss equation given above with  $J=15/2$  were found to be  $g=1.19$  and

$\theta = -2.72$  K with an R-value of 0.0210. This fit shows excellent agreement with the experimental data. All attempts to fit the data to the Curie-Weiss equation with  $J=7$ , both with and without the presence of a noninteracting radical electron, were unsuccessful. The values for  $g$  and  $\theta$  were allowed to vary freely during the SIMPLEX fitting routine, and always converged to the same values as those given above. Therefore, in the case of  $\text{HoPc}_2$ , it is obvious that the ground state for this system is the  ${}^6\text{F}_{11/2}$  state which arises from the strong antiferromagnetic coupling between the holmium f-electrons and the phthalocyanine radical electron. The  ${}^8\text{F}_{13/2}$  excited state which arises from the ferromagnetic coupling as described previously, does not appear to contribute to the magnetism in the temperature range studied.

vi) *Erbium*

From the experimental data taken from 4.2 to 300 K, it can be seen that the magnetic moment levels off near 8.2 B. M. Due to the significant decrease in the experimental magnetic moment from that which is expected for the  ${}^4\text{I}_{15/2}$  ground state, the data were fit to the Curie-Weiss equation assuming an antiferromagnetic interaction between erbium and phthalocyanine electrons. Above 15 K, the data were fit to the model described with a  $g$ -value of 1.124 and a  $\theta$  value equal to -10.66 K. This fit gave an R-value of 0.00983. This data could not be fit to any of the other models described above. At temperatures below 15 K the data could not be fit. The inability to fit the data below 15 K and the slightly low  $g$  value from that which is expected indicate that the effects of the crystal field are not well understood in this case. Further calculations are



necessary.

vii) *Thulium*

The experimental data taken from 4.2 to 300 K does not follow simple Curie-Weiss behavior. At very low temperatures (up to 60 K), the data appears to level off near 6.5 B. M. However, above this temperature, deviations are evident. Due to the inability to fit the data to the Curie-Weiss law with  $J=11/2$ , many attempts were made to fit the data to the  $^3H_6$  state, with and without the presence of the ligand radical electron. All attempts were unsuccessful, ruling out all other possibilities considered. Thus the data was fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state.

As expected, this model does not fit the data at low temperatures, since the model assumes for simplicity that all  $m_j$  states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 30 K, the data can be fit to this model with  $J_0=11/2$ ,  $J_1=13/2$ ,  $g_0$  and  $g_1$  equal to 1.09 and 1.23, respectively, and  $\Delta E$  equal to  $98\text{ cm}^{-1}$ . This fit gave an R-value of 0.01292 with  $T_{\min}$  set at 15 K. Thulium bis(phthalocyanine) is another example in the series of lanthanide bis(phthalocyanine) sandwich compounds that shows the presence of the ferromagnetically coupled excited state and strengthens the validity of the model of the magnetic behavior proposed.

*viii) Ytterbium*

The experimental data taken from 4.2 to 300 K does not follow simple Curie-Weiss behavior. At very low temperatures (up to 60 K), the data begins to level off near 3.4 B. M. The low temperature data were fit to the Curie-Weiss model giving the values  $g=1.04$ ,  $\theta=-4.66$  K, with an R-value for the fit of 0.0186. This model was fit using  $J=3$  and appears to closely resemble the model for strong antiferromagnetic coupling. Above this temperature, deviations are evident.

Due to the inability to fit all of the data to the Curie-Weiss law with  $J=3$ , an attempt was made to fit the data to the  $^2F_{7/2}$  state, with and without the presence of the ligand radical electron. No reasonable fit could be obtained. Thus the data were fit to a model which includes both the antiferromagnetic coupled ground state and the ferromagnetically coupled excited state.

As expected, this model does not fit the data at very low temperatures, since the model assumes for simplicity that all  $m_j$  states are equally populated. This of course is not accurate at low temperatures and depends on the magnitude of the crystal field which exists as a small perturbation for both the antiferro- and ferromagnetically coupled states. At temperatures above approximately 30 K the data can be fit to this model with  $J_0=3$ ,  $J_1=4$ ,  $g_0$  and  $g_1$  equal to 0.95 and 1.25, respectively, and  $\Delta E$  equal to  $125\text{ cm}^{-1}$ . This fit gave an R-value of 0.0401 with  $T_{\min}$  set at 15 K.

Due to the relatively large magnetic dilution in ytterbium bis(phthalocyanine), especially as compared to others in this series, the data are somewhat noisy. Therefore, the accuracy of the fit may be decreased. Several

sets of data were taken and fit in an attempt to improve the validity of the fit and all sets of data, although noisy, led to nearly the same fit values.

Ytterbium bis(phthalocyanine) is another example in this series of compounds which exhibits the presence of both the antiferro- and ferromagnetically coupled states of the lanthanide and phthalocyanine radical electrons. All evidence leads to the conclusion that the model derived here is appropriate in this series of compounds. The data could not be fit to the  $^2F_{7/2}$  free ion state, and no mixing in of the  $^2F_{5/2}$  at  $10,000\text{ cm}^{-1}$  away can possibly exist and can thus be ignored. The possibility that the ytterbium might exist in a state other than its trivalent state was also explored, but none were able to adequately account for the magnetic behavior. It is important to note that the new ground state in this system, a  $^1F_3$  state, with a magnetic moment on the order of 3.6 B. M., contains no formally unpaired electrons. This is the first known example of a complex compound in which magnetism of such a large magnitude can be attributed solely to orbital angular momentum.

#### *ix) Lutetium*

The experimental data for lutetium bis(phthalocyanine) exhibits a limiting moment near 1.75 B.M. The best fit values to the Curie-Weiss law gives a g-value equal to 2.12 with  $\theta = -38.60\text{ K}$  and an R-factor for the fit of 0.05826. Again, the data are noisy due to magnetic dilution (1 spin/1200 amu), but the fit remains valid. The relatively large g and  $\theta$  values are attributed to intercluster interactions between unpaired electrons on adjacent lutetium bis(phthalocyanine) species. This is further validated by the EPR spectra seen for lutetium

bis(phthalocyanine) as discussed later in this text.

### *Electron Paramagnetic Resonance*

When the effects of orbital moment are small, resonances are manifested as small deviations (from  $g_e$ ) in the g-value. This is the case for the free electron which exists in the lutetium bis(phthalocyanine) system which exhibits a g-value of 2.01 at 298 K and a g-value of 2.00 at 7.2 K as seen in Figure 3. The fact that the line width increases as the temperature is lowered is attributed to the intercluster interactions which exist between unpaired electrons on adjacent lutetium bis(phthalocyanine) species. Since spin-spin interactions result from the small magnetic fields that exist on neighboring paramagnetic ions, the total field at the ion is slightly altered and the transition energies appear to be shifted. A distribution of energy results which produces a broadened spectrum. The EPR spectra of lutetium bis(phthalocyanine) show a line width of 1.5 Oe at 298 K and 11 Oe at 7.2 K.

Since the phthalocyanine radical electron which exists in the lanthanide bis(phthalocyanine) compounds (other than lutetium) show very strong coupling with the lanthanide f-electrons, EPR transitions at or near the free electron g value are not expected. Since the new states formed by this coupling contain large uncompensated orbital angular momentum, the deviations from  $g_e$  are expected to be very significant. As discussed earlier, strong spin-orbit coupling interactions exist in most lanthanide compounds and therefore, J remains a good quantum number. After this, the ligand field splitting is treated as a perturbation to the J states. EPR transitions in these systems occur between crystal field states or between states such as Kramer's doublets, which are split only in a magnetic

field.

The EPR spectra of the lanthanide bis(phthalocyanine) compounds where the lanthanide is praseodymium, gadolinium, dysprosium, holmium, erbium, thulium or ytterbium show very complicated EPR spectra with no transitions at or near  $g=2$ , except for the spectrum of praseodymium bis(phthalocyanine) in which the transition at  $g=2$  may simply be fortuitous. However, the very complicated task of calculating the crystal field effects in these systems is necessary in order to adequately interpret the EPR spectra in these systems. This work is currently underway.

#### *Pathways For Exchange*

Two possible mechanisms exist to explain the phenomenon of spin-spin coupling interactions. The first possibility is direct contact between adjacent magnetic orbitals. The second possibility is superexchange, where the magnetic orbitals overlap with filled orbitals and are delocalized in this manner. The rules which govern the exchange depend on the occupancy and symmetry of the orbitals involved [25].

If there is finite overlap of the magnetic orbitals on adjacent species, then according to the Pauli principle, the spins must be aligned antiparallel. The spins are paired and the exchange is antiferromagnetic. Anderson [26] has labelled this as kinetic exchange. When the magnetic orbitals are orthogonal, their spins are aligned parallel and the exchange is ferromagnetic. Anderson has labelled this as potential exchange. A magnetic orbital on one ion may also overlap with an empty orbital on a second magnetic ion. Intra-atomic coupling of the electrons in these orthogonal magnetic orbitals is also ferromagnetic.

Calculations indicate that  $J_{ij}(\text{kinetic}) \gg J_{ij}(\text{potential})$ , and therefore when both kinetic and potential exchange are possible the kinetic contribution is usually the largest.

If there is little direct overlap of magnetic orbitals, finite exchange across filled d-orbitals plays an intermediary role in the exchange between magnetic ions. Finite overlap of both magnetic orbitals with the intermediate filled d-orbitals would lead to antiferromagnetic exchange coupling as described above. Overlap of one magnetic ion with the filled d-orbitals, which in turn is adjacent to an orthogonal orbital on the other magnetic ion or overlaps with an empty orbital on that ion, would lead to a ferromagnetic contribution to the exchange.

The  $\pi$  molecular orbitals of metal-free phthalocyanine were obtained by Chen [27] using Hückel-type Molecular Orbital calculations. Although the symmetry of the phthalocyanine in Chen's study was assumed to be  $D_{2h}$ , it is easily converted into  $C_{4v}$  symmetry as necessary for this study. The symmetry of the HOMO of phthalocyanine which contains the unpaired electron is  $a_u$ . It is assumed that the iso-indoline (inner) nitrogens play the key role in bonding and electron exchange in these lanthanide bis(phthalocyanine) compounds. The linear combination of atomic orbitals (LCAOs) for the iso-indoline nitrogens is

$$\psi = N_a - N_b + N_c - N_d$$

where a-d consecutively label the four inner nitrogens on the phthalocyanine. When the LCAOs of the two phthalocyanines are combined in the symmetry appropriate for the lanthanide bis(phthalocyanine) compounds, two new molecular orbitals arise. These two orbitals transform as  $b_1$  and  $b_2$  in  $C_{4v}$

symmetry as described below.

The two phthalocyanines are designated as "Ring A" and "Ring B". These two rings can be combined in two configurations, "A + B" and "A - B" as depicted in Figure 4, and the two new molecular orbitals formed from this combination transform as  $b_1$  and  $b_2$  in  $C_{4v}$  symmetry.

Based on the geometry of the f-orbitals as depicted by Becker [28] the splitting of the f-orbitals in  $C_{4v}$  symmetry can be determined. It can be seen that  $f_{xyz}$  lies highest in energy since 4 of 8 lobes point directly toward the 4 inner nitrogens on one of the phthalocyanine ligands. The  $f_{z(x^2-y^2)}$  orbital, although very close in energy to the  $f_{xyz}$  orbital, is slightly lower in energy since the second phthalocyanine is rotated only  $42^\circ$  and therefore 4 of 8 lobes are not directly pointed toward the phthalocyanine nitrogens. Both the  $f_{x(z^2-y^2)}$  and  $f_{y(z^2-x^2)}$  have two of 8 lobes which are directed toward the phthalocyanine nitrogens. Therefore, they are of lower energy than the  $f_{z(x^2-y^2)}$  orbital, but still higher in energy than  $f_{z^3}$ ,  $f_{x^3}$  and  $f_{y^3}$  set in which no lobes are pointed at or near the phthalocyanine nitrogens. The ( $f_{z^3}$ ,  $f_{x^3}$ ,  $f_{y^3}$ ) set are slightly split in energy since the two phthalocyanines are not centrosymmetric and therefore the  $f_{z^3}$  orbital is slightly higher in energy than the  $f_{x^3}$  and  $f_{y^3}$  orbitals.

Based on the arguments given above, the splitting of d-orbitals in  $C_{4v}$  symmetry is also easily determined. However, since all of the 4d-orbitals of the lanthanides are filled, the exact energy of each of the orbitals is not as significant as the symmetry which they possess.

## Conclusion

Since the unpaired electron from the phthalocyanine ligands lies in the molecular orbital with  $B_2$  symmetry, interaction with the  $B_2$  orbital of the f-orbital set would lead to magnetic exchange. Since the  $f_{xyz}$  orbital of the f set possesses  $B_2$  symmetry and is highest in energy, it is a magnetic orbital (one unpaired electron) as long as the f-electron shell is more than half-filled. This is the case for the lanthanides gadolinium through ytterbium and therefore leads to antiferromagnetic exchange in these systems. In the case of praseodymium, the less than half-filled f-electron shell leaves the  $B_2$  orbital empty and therefore leads to a ferromagnetic coupling with the phthalocyanine radical electron.

Likewise, if the d-orbitals are involved, overlap is possible between the  $B_2$  orbital of the phthalocyanine radical and the filled  $B_2$  orbital ( $d_{xy}$ ) of the 4d set which in turn overlaps with the  $B_2$  orbital of the f-orbital set. If the  $B_2$  orbital of the f-orbital set contains one unpaired electron then the exchange is antiferromagnetic, as is the case for gadolinium through ytterbium. If the  $B_2$  orbital of the f-orbital set is empty then the exchange is ferromagnetic, as is the case for praseodymium. Thus, the pathways for exchange based on orbital symmetry and occupancy are able to describe the magnetic behavior of the lanthanide bis(phthalocyanine) compounds as seen previously.

## Acknowledgements

This work was funded by the Office of Naval Research, the Department of Education and the National Science Foundation.



## References

- 1 See, for example, G. A. Melson, *Coordination Chemistry of Macrocyclic Compounds*, Plenum Press, New York, 1979.
- 2 a) J. W. Buchler, K. Elsasser, M. Kihn-Botulinski and B. Scharbert, *Angew. Chem. Int. Ed. Engl.*, **25** (1986) 286. b) J. W. Buchler and B. Scharbert, *J. Am. Chem. Soc.*, **110** (1988) 4272. c) J. W. Buchler and M. Knoff, *Opt. Prop. Struct. Tetrapyrroles; Proc. Symp.* (1984) 91.
- 3 (a) P. N. Moskalev and I. S. Kirin, *Russian J. Inorg. Chem.*, **15** (1970) 7. (b) P. N. Moskalev, I. S. Kirin and Y. A. Makashev, *Russian J. Inorg. Chem.*, **10** (1965) 1065.
- 4 A. Decian, M. Moussavi, J. Fischer, and R. Weiss, *Inorg. Chem.*, **24** (1985) 3162.
- 5 (a) A. Gieren and W. Hoppe, *Chem. Comm.* (1971) 413. (b) K. Kasuga, M. Tsutsui, R. C. Petterson, K. Tatsumi, N. Van Opdenbosch, G. Pepe and E. F. Meyer, Jr. *J. Amer. Chem. Soc.*, **102** (1980) 4836. (c) A. N. Darovskikh, private communications.
- 6 I. S. Kirin, P. N. Moskalev, and Y. A. Makashev, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **10** (1965) 1065 and **12** (1967) 369.
- 7 C. Clarisse and M. T. Riou, *Inorg. Chim. Acta*, **130** (1987) 139.
- 8 A. G. MacKay, J. F. Boas and G. Troup, *J. Aust. J. Chem.*, **27** (1974) 955.
- 9 I. S. Kirin, P. N. Moskalev and N. V. Ivannikova, *Russ. J. Inorg. Chem. (Engl. Transl.)*, **12** (1967) 497.
- 10 P. N. Moskalev and G. N. Shapkin, *Elektrokhimiya*, **14** (1978) 574.

- 11 P. N. Moskalev, G. N. Shapkin, and A. N. Darovskikh, *Russ. J. Inorg. Chem.*, **24** (1979) 188.
- 12 G. A. Corker, B. Grant and N. J. Clecak, *J. Electrochem.*, **126** (1979) 1339.
- 13 A. T. Chang and J.-C. Marchon, *Inorg. Chim. Acta*, **53** (1981) L241.
- 14 B. N. Figgus and R. S. Nygolm, *J. Chem. Soc.* (1959) 548.
- 15 D. B. Brown, V. H. Crawford, V. H., J. H. Hall, and W. E. Hatfield, *J. Phys. Chem.*, **81** (1977) 1303.
- 16 H. Rade, *J. Phys. Chem.*, **77** (1973) 424.
- 17 B. N. Figgis, and J. Lewis, in R. Wilkins (ed.), *Modern Coordination Chemistry*, Wiley-Interscience, New York, 1960.
- 18 E. König, *Magnetic Properties of Transition Metal Compounds*, Springer-Verlag, West Berlin, 1966.
- 19 W. Spendley, G. R. Hext, and F. R. Himsworth, *Technometrics*, **4** (1962) 441.
- 20 J. A. Nelder and R. Mead, *Computer J.*, **7** (1965) 308.
- 21 R. O'Neill, *Appl. Stat.*, **20** (1971) 338.
- 22 D. Markovitsi, T.-H. Tran-Thi, R. Even, and J. Simon, *Chem. Phys. Letters*, **137** (1987) 107.
- 23 A. N. Darovskikh, A. K. Tsytchenko, O. V. Frank-Kamenetskaya, V. S. Fundamenskii and P. N. Moskalev, *Sov. Phys. Crystallogr. (Engl. Trans.)*, **29** (1984) 273.
- 24 A. De Cian, M. Moussavi, J. Fischer, and R. Weiss, *Inorg. Chem.*, **24** (1985) 3162.
- 25 W. E. Hatfield, in E. A. Boudreaux and L. N. Mulay (eds.), *Theory and Applications of Molecular Paramagnetism*, Wiley-Interscience, New York, 1976.

- 26 P. W. Anderson, *Phys. Rev.*, *115* (1959) 2.
- 27 I. Chen, *J. Mol. Spec.*, *23* (1967) 131.
- 28 C. Becker, *J. Chem. Ed.*, *41* (1964) 358.

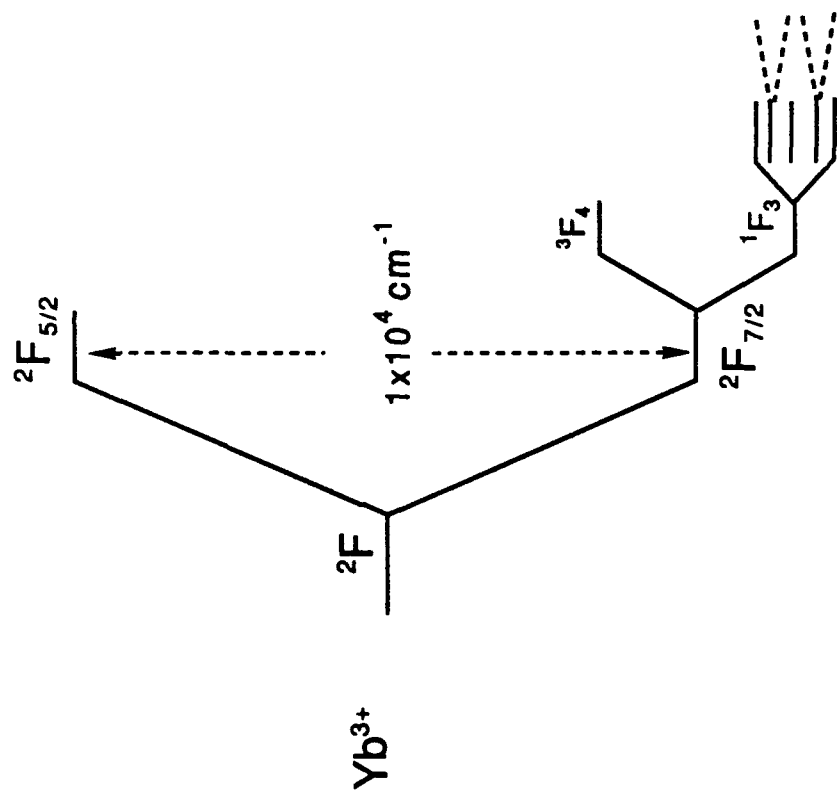
**Figure Captions:**

Figure 1: A model of the energy level splitting for the lanthanide ions, including a strong interaction with the phthalocyanine ligand radical, with  $\text{Yb}^{3+}$  given as the example.

Figure 2: The experimental magnetic susceptibility data, given in units of  $\mu_{\text{eff}}$  versus temperature, for all of the lanthanide bis(phthalocyanine) sandwich compounds studied.

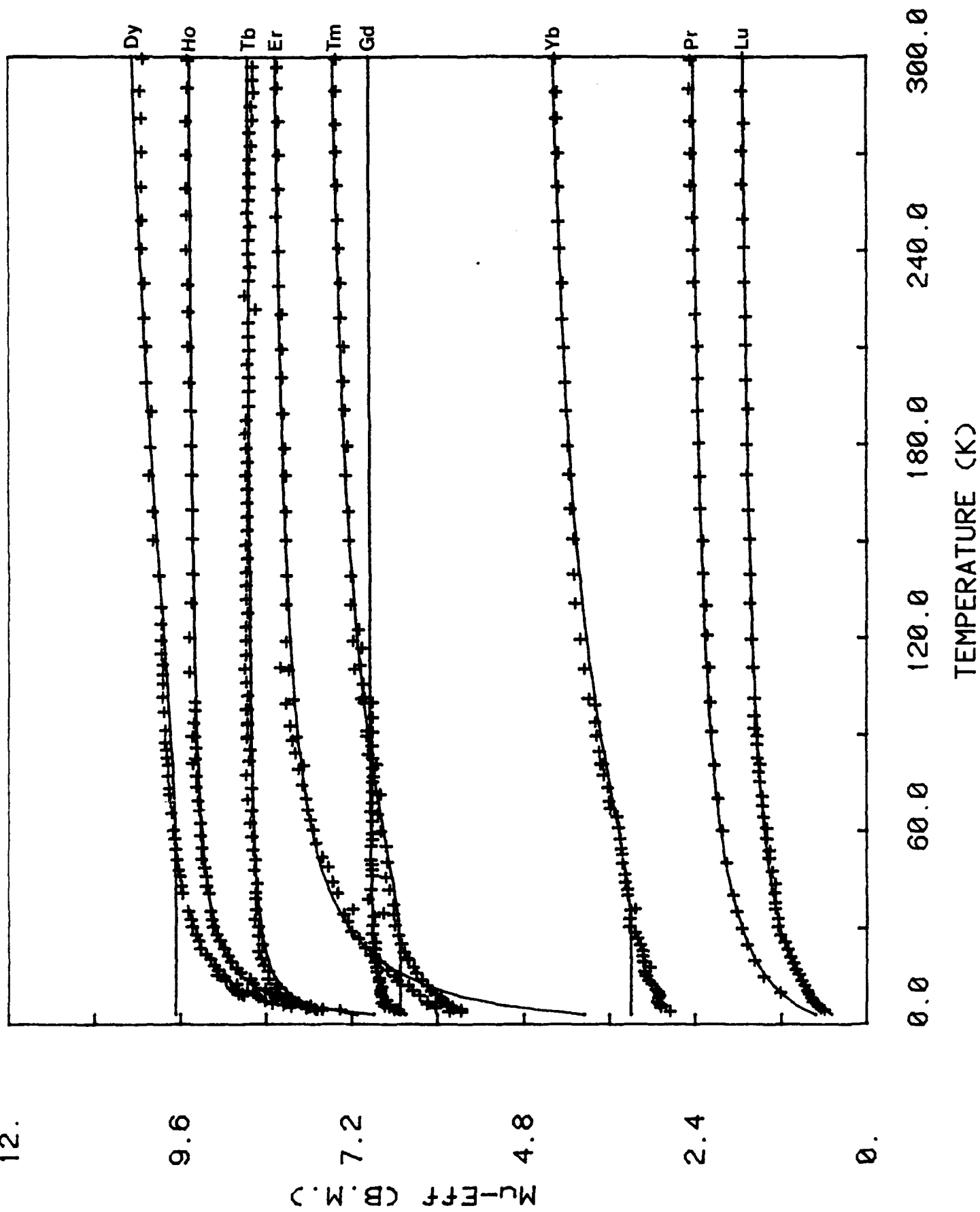
Figure 3: The EPR spectra of lutetium bis(phthalocyanine) at 298 K and 7.2 K.

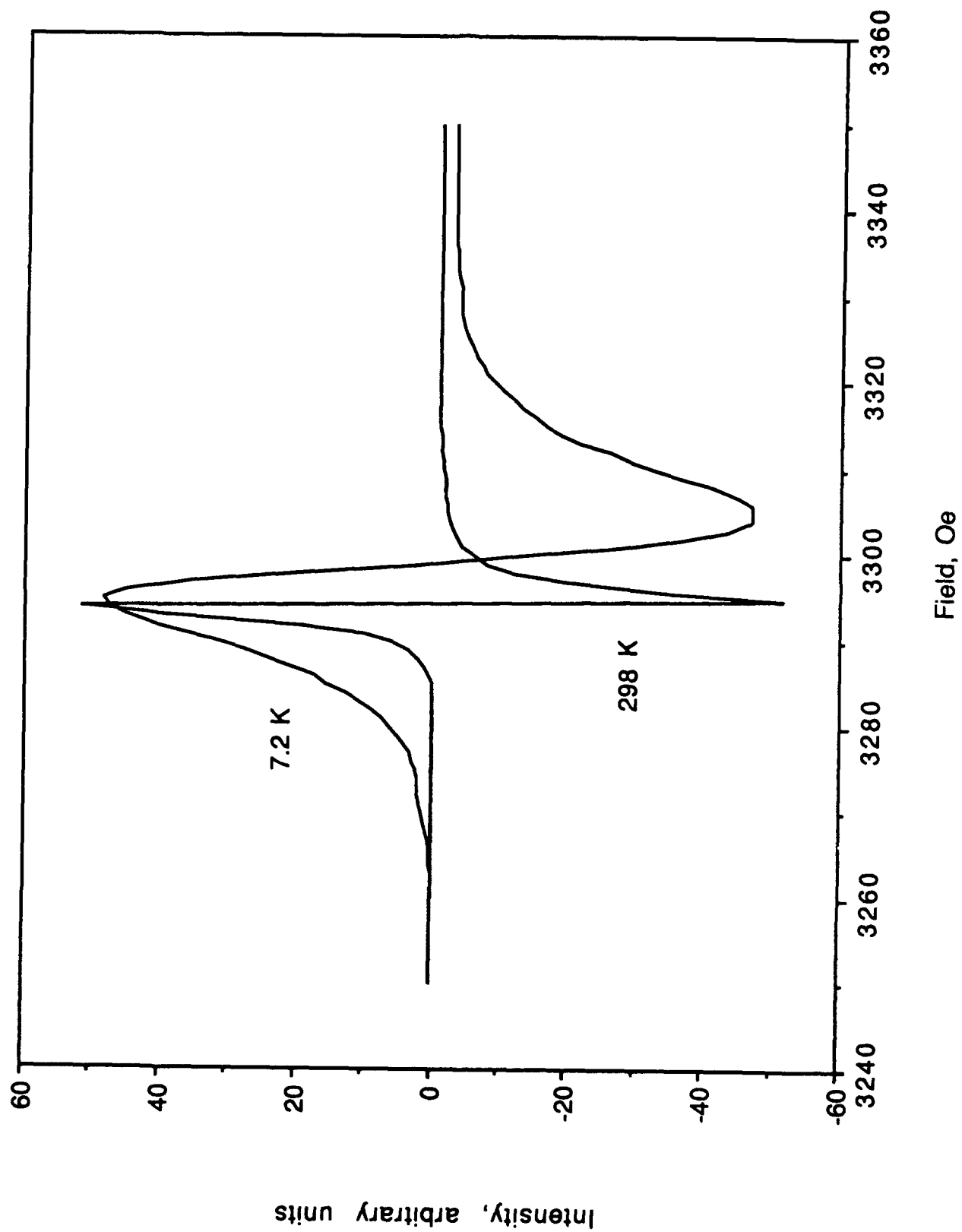
Figure 4: Schematic diagram of the LCAOs formed from the iso-indoline nitrogens for the two phthalocyanine ligands in the lanthanide bis(phthalocyanine) sandwich compounds.

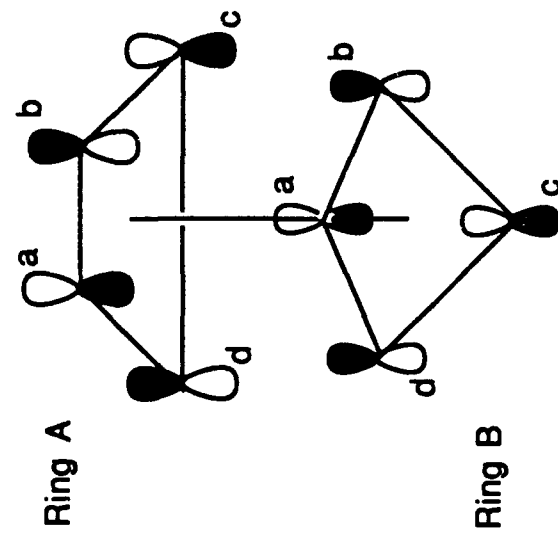
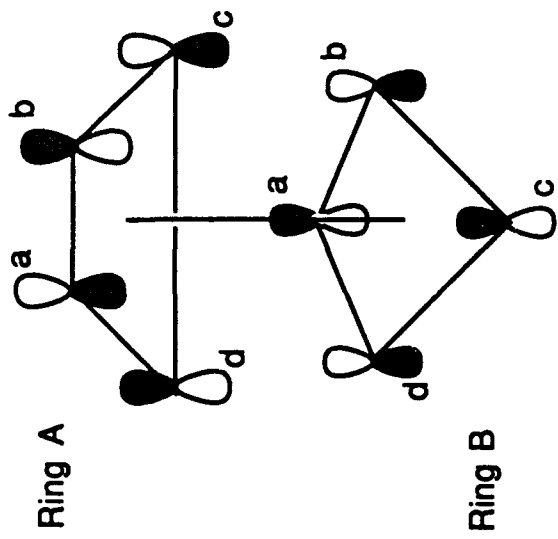


free ion +  $\lambda L S$  +  $^2S_{1/2}$  +  $C_{4v}$  + magnetic field

12.









**Table 1:** Ultraviolet, visible and near infrared transitions (in nm) for the lanthanide bis(phthalocyanine) sandwich compounds.

$\text{LnPc}_2$	Soret <sup>1</sup> $e_g \rightarrow a_{1u}$ <sup>2</sup>	Q-band <sup>1</sup>	$e_g \rightarrow a_{1u}$ <sup>2</sup>	CTI <sup>3</sup>
LuPc <sub>2</sub>	320	658	917	1370
YbPc <sub>2</sub>	322	660	917	1386
TmPc <sub>2</sub>	320	660	915	1390
ErPc <sub>2</sub>	322	662	913	1397
HoPc <sub>2</sub>	322	664	913	1406
DyPc <sub>2</sub>	322	666	914	1416
TbPc <sub>2</sub>	322	666	909	1419
GdPc <sub>2</sub>	322	670	912	1424
PrPc <sub>2</sub>	<300	678	898	1770

<sup>1</sup> Q- and Soret bands from dianionic form of phthalocyanine.

<sup>2</sup> Transitions due to "hole" in HOMO of monoanionic phthalocyanine.

<sup>3</sup> Intervalence charge transfer bands  $\text{Pc}^{2-} \rightarrow \text{Pc}^{1-}$ .

**Table 2:** Theoretical values of  $\mu_{\text{eff}}$  (in B. M.) for all of the trivalent lanthanides using the free ion term and the free ion plus radical term, as discussed in the text, as compared to the limiting values found experimentally for the lanthanide bis(phthalocyanine) sandwich compounds.

<b><u>LnPc<sub>2</sub></u></b>	<b><u>Lanthanide Free Ion</u></b>	<b><u>Lanthanide-Radical Interaction</u></b>		<b><u>Limiting Value Experimental</u></b>
		<b><u>None</u></b>	<b><u>Ferromagnetic Antiferromagnetic</u></b>	
PrPc <sub>2</sub>	3.58	3.97	2.65 4.52	2.5
GdPc <sub>2</sub>	7.94	8.12	8.94 6.93	6.9
TbPc <sub>2</sub>	9.72	9.87	10.75 8.70	8.6
DyPc <sub>2</sub>	10.63	10.76	11.67 9.62	10.2
HoPc <sub>2</sub>	10.60	10.75	11.59 9.58	9.5
ErPc <sub>2</sub>	9.57	9.74	10.61 8.55	8.2
TmPc <sub>2</sub>	7.63	7.78	8.59 6.52	7.2
YbPc <sub>2</sub>	4.52	4.84	5.59 3.46	4.3
LuPc <sub>2</sub>	0	1.73	--- ---	1.7

TECHNICAL REPORT DISTRIBUTION LIST, GENERAL

	<u>No. Copies</u>		<u>No. Copies</u>
Office of Naval Research Chemistry Division, Code 1113 800 North Quincy Street Arlington, VA 22217-5000	3	Dr. Ronald L. Atkins Chemistry Division (Code 385) Naval Weapons Center China Lake, CA 93555-6001	1
Commanding Officer Naval Weapons Support Center Attn: Dr. Bernard E. Douda Crane, IN 47522-5050	1	Chief of Naval Research Special Assistant for Marine Corps Matters Code OOMC 800 North Quincy Street Arlington, VA 22217-5000	1
Dr. Richard W. Drisko Naval Civil Engineering Laboratory Code LS2 Port Hueneme, California 93043	1	Dr. Bernadette Eichinger Naval Ship Systems Engineering Station Code 053 Philadelphia Naval Base Philadelphia, PA 19112	1
Defense Technical Information Center Building 5, Cameron Station Alexandria, Virginia 22314	2 <u>high</u> <u>quality</u>	Dr. Sachio Yamamoto Naval Ocean Systems Center Code 52 San Diego, CA 92152-5000	1
David Taylor Research Center Dr. Eugene C. Fischer Annapolis, MD 21402-5067	1	David Taylor Research Center Dr. Harold H. Singerman Annapolis, MD 21402-5067 ATTN: Code 283	1
Dr. James S. Murday Chemistry Division, Code 6100 Naval Research Laboratory Washington, D.C. 20375-5000	1		

# Abstract Distribution List

Professor O. T. Beachley, Jr.  
Department of Chemistry  
State University of New York  
Buffalo, NY 14214

Dr. Alan Berry  
Chemistry Division, Code 6120  
Naval Research Laboratory  
4555 Overlook Ave. SW  
Washington, DC 20375-5000

Professor Jerald S. Bradshaw  
Department of Chemistry  
Brigham Young University  
Provo, UT 84602

Professor Ronald Breslow  
Department of Chemistry  
Columbia University  
New York, NY 10027

Dr. Duncan W. Brown  
Advanced Technology Materials, Inc.  
520-B Danbury Rd.  
New Milford, CT 06776

Professor Herbert C. Brown  
Purdue University  
Department of Chemistry  
West Lafayette, IN 47907

Professor Steven L. Buchwald  
Department of Chemistry  
Massachusetts Institute of Technology  
Cambridge, MA 02139

Professor Cynthia J. Burrows  
Department of Chemistry  
State University of New York  
Stony Brook, NY 11794-3400

Dr. Roque J. Calvo  
Executive Secretary  
The Electrochemical Society  
10 South Main St.  
Pennington, NJ 08534-2896

Professor Peter Chen  
Department of Chemistry  
Harvard University  
Cambridge, MA 02138

Professor N. John Cooper  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260

Professor Anthony W. Czarnik  
Department of Chemistry  
Ohio State University  
120 West 18th Ave.  
Columbus, OH 43210-1173

Professor Peter Dervan  
Department of Chemistry  
California Institute of Technology  
Pasadena, CA 91125

Professor Francois N. Diederich  
Department of Chemistry  
University of California  
405 Hilgard Ave.  
Los Angeles, CA 90024

Professor Dennis A. Dougherty  
Department of Chemistry  
California Institute of Technology  
Pasadena, CA 91125

Professor Kenneth M. Doxsee  
Department of Chemistry  
University of Oregon  
Eugene, OR 97403

Dr. Regis J. Ebner, Jr.  
Director of Finance  
Materials Research Society  
9800 McKnight Rd., Ste. #27  
Pittsburgh, PA 15237

Professor Margaret C. Etter  
Department of Chemistry  
University of Minnesota  
207 Pleasant St., S.E.  
Minneapolis, MN 55455

Professor Wilmer K. Fife  
Department of Chemistry  
Indiana University-Purdue University at  
Indianapolis  
1125 East 38th St.  
PO Box 647  
Indianapolis, IN 46223

Professor Samuel H. Gellman  
Department of Chemistry  
1101 University Ave.  
Madison, WI 53706

Professor Andrew D. Hamilton  
Department of Chemistry  
University of Pittsburgh  
Pittsburgh, PA 15260

Professor William E. Hatfield  
Department of Chemistry  
University of North Carolina  
Chapel Hill, NC 27514

Dr. Kelvin Higa  
Chemistry Division  
Research Department  
Naval Weapons Center  
China Lake, CA 93555

Professor Kenneth D. Karlin  
Merry Hall 146  
The Johns University  
34th & Charles Streets  
Baltimore, MD 21218

Professor Arthur E. Martell  
Department of Chemistry  
Texas A&M University  
College Station, TX 77843-3255

Professor Thomas J. McCarthy  
Department of Polymer Science  
University of Massachusetts  
Rm. 701 Graduate Research Center  
Amherst, MA 01003

Dr. Stephen W. McElvany  
Code 6113, Chemistry Division  
Naval Research Laboratory  
Washington, DC 20375-5000

Professor Lisa McElwee-White  
Department of Chemistry  
The Leland Stanford Junior University  
Stanford, CA 94305

Dr. Theodore G. Pavlopoulos  
Naval Ocean Systems Center  
Code 521 (B-111)  
San Diego, CA 92152-5000

Professor William S. Rees, Jr.  
Chemistry Division  
The Florida State University  
Tallahassee, FL 32306-3006

Professor Peter Schultz  
Department of Chemistry  
University of California  
Berkeley, CA 94720

Dr. Alok Singh  
Center for Bio/Molecular Science  
Engineering  
Department of the Navy  
Naval Research Laboratory, Code 6090  
Washington, DC 20375-5000

Dr. Michael L. Sinnott  
University of Bristol  
School of Chemistry  
Cantock's Close  
Bristol  
ENGLAND BS8 1TS

Dr. Timothy M. Swager  
Department of Chemistry  
University of Pennsylvania  
Philadelphia, PA 19104-6323

Professor Richard L. Wells  
Department of Chemistry  
Duke University  
Durham, NC 27706

Professor Jeffrey D. Winler  
Department of Chemistry  
The University of Pennsylvania  
133 South 36th St.  
Philadelphia, PA 19104-3246

Professor Jeffrey D. Zubkowski  
Department of Chemistry  
Jackson State University  
PO Box 17910, 1400 Lynch St.  
Jackson, MS 39217